Block Copolymer Domain Reorientation in an Electric Field: An *In-Situ* Small-Angle X-ray Scattering Study

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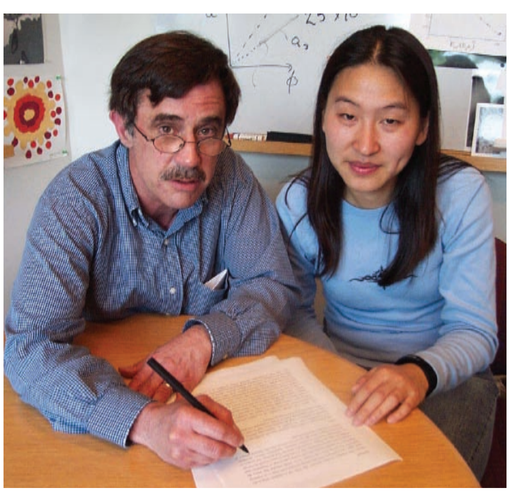
The electric field alignment of block copolymer thin films from an orientation nearly parallel to the substrate to an orientation normal to the substrate was investigated using in-situ small angle x-ray scattering (SAXS). An analysis of the scattering patterns indicated that, during alignment of the lamellar microdomains, the material goes through an intermediate state with substantially reduced order. After orientation, the sample consists of many small grains with the lamellae oriented parallel to the electric field and a random orientation in the plane perpendicular to the field.

Block copolymers, comprised of two chemically distinct polymers covalently linked at one end, self-assemble into well-ordered arrays of nanoscopic elements, ranging from spheres to cylinders to lamellae, depending on the volume fraction of the components. The size of the domains can be easily tuned by varying the molecular weight of the copolymer. However, it is imperative to control the orientation of these self-assembled morphologies, and the use of an external electric field has proven to be an effective method to achieve this. Nanoporous films with aspect ratios in excess of 300 have been successfully made by orienting the domains in thin block copolymer films and selectively removing one component. The subsequent electrodeposition of metal into these nanopores produces arrays of high-aspect ratio nanowires that are attracting substantial attention as candidates for high-density magnetic storage media. Understanding the mechanism by which the nanoscopic domains are aligned by an electric field is the key to optimizing their use.

Figure 1 shows the orientation of cylindrical domains of a diblock copolymer under an applied electric field. Starting from an ordered state with cylinders parallel to the surface, the applied electric field enhances fluctuations at the interfaces between the domains and at the matrix where the fluctuations have a wavelength comparable to L_o, the center-to-center distance between the cylindrical domains. The enhancement in the fluctuations leads to a disruption of cylindrical domains, the formation of spherical domains, the deformation of these spherical domains into ellipsoids, and the eventual reformation of nanoscopic cylinders highly oriented in the field direction. In-situ small angle x-ray scattering (SAXS) provides an ideal means of characterizing the orientation of the domains and elucidating the mechanism by which the orientation occurs. Two different copolymers were studied: one with cylindrical domains and the other with lamellar nanoscopic domains. Here, we discuss the orientation of lamellae due to geometric simplicity.

Figure 2 shows the azimuthal angular (Ω) dependence of the



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Beamline X10A

Funding
U.S. Department of Energy, Office of Basic Energy Sciences; Army Research Lab; National Science Foundation – Materials Research Science and Engineering Center

Publication
J. DeRouchey, T. Thurn-Albrecht, R. Kolb, and T.P. Russell, "Block Copolymer Domain Reorientation in an Electric Field: An *in-Situ* Small-Angle X-ray Scattering Study", *Macromolecules*, **37**(**7**), 2538 (2004).

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time-resolved SAXS pattern of an ordered, symmetric diblock copolymer, polystyrene-*b*-polyisoprene film (~ 80-120μm in thickness), that was heated above the glass transition temperature of both blocks under an applied electric field. Four distinct SAXS patterns were seen in the experiments that characterized different stages of the orientation. The sequence of patterns (**A-D**) arises from the re-orientation of the lamallar domains from nearly parallel to the substrate (**A, B**) to normal to the substrate (**D**). Curve **C**, however, revealed an unexpected result in which the azimuthal dependence of the SAXS was lost. This, coupled with a shift in the peak to higher scattering vectors (smaller spacing) and a broadening of the peak, suggests, contrary to the results from simulations, that the block copolymer domains disorder or are broken-up, and then reform in the presence of the field. These reformed domains are highly oriented in the direction of the applied field. Thus, the time-resolved SAXS pattern revealed an unexpected disordering of the copolymer.

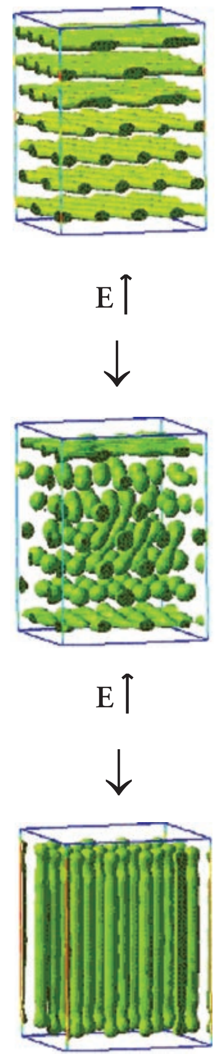

Figure 1. Simulation of the alignment of cylindrical microdomains under an electric field based on the dynamic self-consistent field (courtesy of A. Zvelindovsky).

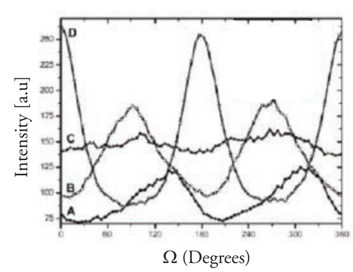

Figure 2. Azimuthal angular dependence of the scattering pattern integrated over the full width of the Bragg reflection of a lamellar PS-*b*-PI film under an 18 V/μm applied field. The film is tilted at a 45° angle. Four distinct SAXS patterns (A-D) are shown.